EXAFS Studies of Honheme Iron Enzymes	X9B

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X-ray absorption spectroscopy has been very useful for characterizing the structures of metalloproteins and unstable inorganic species. In our last two runs of the EXAFS experiments in NSLS from October 1997 to June 1998, we have obtained significant results on (a) the membrane-bound alkane hydroxylase AlkB in both reduced and oxidized states, (b) synthetic iron peroxo and high valent iron species relevant to the oxygen activation mechanism of the nonheme iron enzymes, (c) a copper protein associated with Wilson disease.

The XAS studies of oxidized and reduced AlkB indicates that diiron centers in the active site have a histidine-rich ligand environment which is contrast to the carboxylate-rich sites of the soluble diiron enzymes MMO and RNR. It also suggests the presence of a hydroxo bridge in oxidized AlkB instead of the oxo bridge proposed from Mvssbauer results. In our effort to model intermediate species of nonheme iron enzymes, we have obtained EXAFS data on an iron(III)-peroxo intermediate and are able to observe a short Fe-N/O bond at 1.8 Å, presumably associated with the Fe-peroxo bond. Data was also taken and analyzed on bis(mu-oxo) high valent diiron complexes which serve as models of the intermediates Q in MMO and X in RNR. Our preliminary analysis of the Wilson disease protein suggests that the Cu(I) centers are likely to be coordinated by both Cys and His residues, a coordination environment which is distinct from that of the copper chaperone Atx1, to which there is some sequence homology.